

Stable Heptamethine Pyrylium Dyes

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Stable Heptamethine Pyrylium Dyes That Absorb in the Infrared

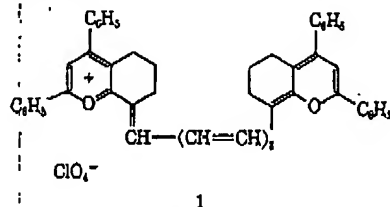
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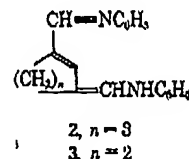
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The stability of heptamethine pyrylium dyes has been greatly increased by incorporating all but two of the methine groups in rings. The effect of ring size and a chlorine atom in the center of the methine chain on the absorption maxima of the dyes is described. By the suitable choice of these factors, a dye which absorbs at about 1.2 μ was obtained. Heptamethine pyrylium dyes were prepared from an indene-1,3-dialdehyde derivative as well as the corresponding 3-chloro derivative. These dyes were not as stable nor did they absorb at as long wavelengths as other similar dyes containing five- and six-membered rings at the center of the methine chain. It has been shown that heptamethine pyrylium dyes containing only the three central methine groups in a ring are as stable as the dyes that contain all but two of the methine groups in rings, and that a thiopyrylium homologue is the most stable heptamethine dye that we have prepared.

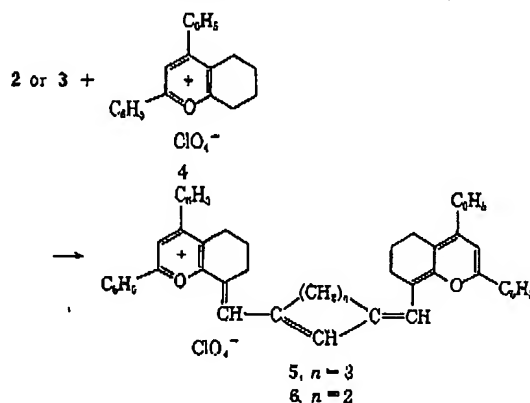
For many years, chemists have been interested in preparing dyes that show electronic absorptions further into the infrared region of the spectrum than existing dyes, and cyanine dyes have proved to be exceptionally useful in this respect. The work with cyanine dyes has been reviewed.¹ A particularly useful route to infrared-absorbing dyes has taken advantage of the fact that the pyrylium nucleus, compared to other heterocyclic nuclei, gives large bathochromic shifts when incorporated in polymethine dyes.² For example, the relatively simple dye 1 (in methylene chloride) shows absorption at 1040 nm with ϵ 125 000.



The present paper describes more recent work on preparing polymethine pyrylium dyes that absorb in the infrared. The successful preparation of 1 depended on partially rigidizing the polymethine chain by incorporating two of the methine groups in rings. Attempts to prepare the pyryloheptamethine dye without these rings were unsuccessful. Evidently, we have reached the limits of stability with 1, since the next higher vinyllog could not be prepared. This result was not surprising because the stability of 1, although much better than that of other polymethine dyes absorbing in this region of the spectrum, is still not good. It was apparent that the most obvious way to increase the stability of 1 or prepare higher vinyllogs would be to incorporate more methine groups in rings. Unfortunately, the reported methods¹ for doing this failed with



pyrylium dyes. It was, therefore, with interest that we noted the recent preparation³ of 2 and 3, which have been used by Russian workers to prepare some pyrylium, thiopyrylium, and selenopyrylium dyes.⁴ We have used these bisaldehyde derivatives to prepare heptamethine dyes 5 and 6 which contain all but two of the methine groups in rings.



The λ_{\max} of 5 and 6, 1090 nm (ϵ 140 000) and 1188 (70 000), respectively, illustrate two characteristics that are common to dyes of this type, namely, that the dyes containing five-

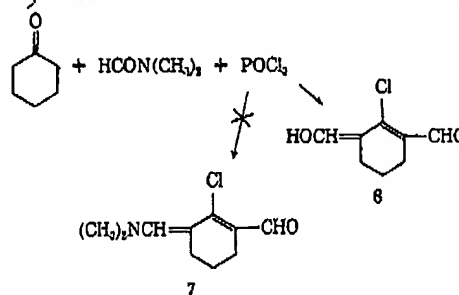
Table I. Polymethine Dyes

<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <p>$A, n = 3$ $B, n = 2$</p> </div> <div style="text-align: center;"> <p>$A', n = 3$ $B', n = 2$</p> </div> </div>			
Dye structure	Compd	λ_{max}, nm ($\epsilon \times 10^{-3}$)	Rel stability
$A=CH-(CH=CH)-A'$	1	1040 (125.0)	1
	5	1090 (140.0)	76
	6	1188 (70.0)	37
	10	1120 (113.0)	128
	11	1145 (143.0)	178
	12	1152 (120.0)	190
	13	1180 (95.0)	49
	14	1120 (111.0)	170
	15	1072 (107.0)	78
	18	1042 (185.0)	7.6
	19	1040 (175.0)	8.7
	24	1125 (112.0)	201

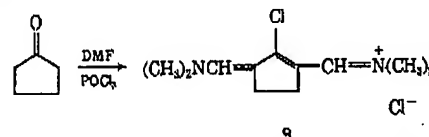
membered rings absorb at longer wavelengths than those with six-membered rings but sometimes with a decrease in the extinction coefficient, and the presence of the central ring results in a bathochromic shift compared to the dye with hydrogen atoms at the 3 and 5 positions of the methine chain (compare λ_{max} of 1 with 5 and 6). The effect of chain substituents on the absorption of polymethine dyes is very interesting. Reichardt has investigated extensively the effect of substituents at the central carbon atom of various pentamethine cyanine dyes and found that electron-withdrawing groups give large shifts to shorter wavelengths.⁶ This can be

understood on the basis of the electron gas model for the π -electron system of cyanine dyes.⁶ The sign of the absorption shift should depend on the number of double bonds (even or odd) between the end groups of the dye. Therefore, we can expect a shift toward longer wavelengths if an electron-withdrawing substituent is introduced at the central carbon atom of a heptamethine dye. Substitution of the hydrogen atom at the central carbon atom of 1, 4, or 5 by a more electronegative atom should result in a bathochromic shift of the dye.

To test this prediction, it was necessary to prepare a suitably substituted bisaldehyde as a precursor to the dye. For this purpose, the work of Zemlicka and Arnold⁷ was repeated. It was reported⁷ that cyclohexanone reacted with the Vilsmeier-Haack reagent to give 7, but we consistently obtained

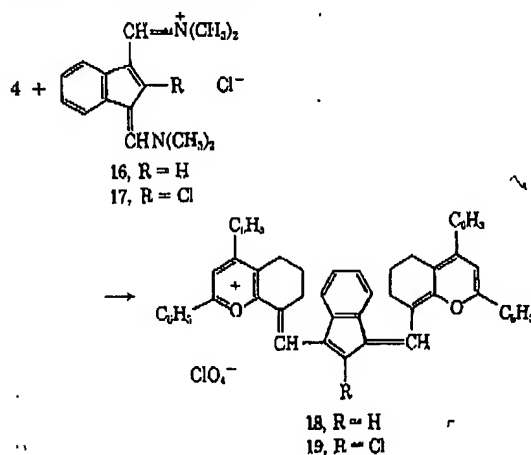


8 as the product. The formation of 9 from cyclopentanone was substantiated. Since 8 and 9 are readily prepared in high yield, they served as ideal starting materials for the synthesis of polymethine dyes bearing a chlorine atom as an electron-withdrawing group on the central carbon of the methine chain.



The dyes prepared from 8 and 9 and their long-wavelength absorptions (in methylene chloride) are shown in Table I. It is seen that substantial bathochromic shifts were obtained by replacing the methine hydrogen with the weakly electronegative atom, chlorine, and also by incorporating five-membered rings throughout the dye.

Arnold has described⁹ the preparation of two additional cyclic bisaldehyde derivatives 16 and 17 that we have used to prepare the rigidized dyes 18 and 19.

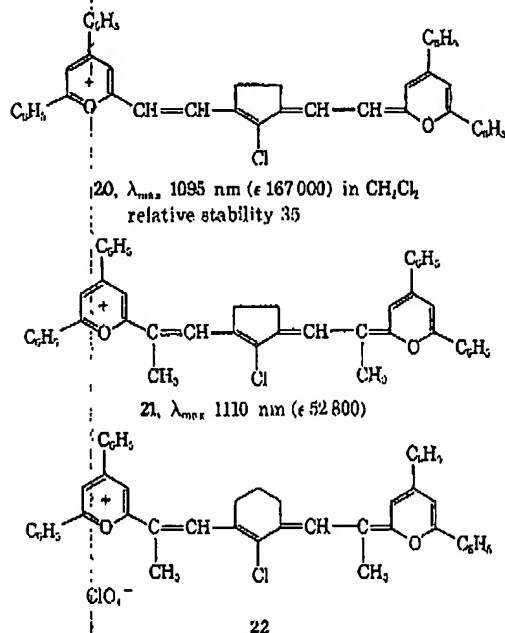


Stable Heptamethine Pyrylium Dyes

The dyes 18 and 19 differed from the corresponding dyes 5 and 6 in that the λ_{max} of 18 and 19 are at shorter wavelengths and the chlorine atom did not cause a shift to longer wavelengths. The exact values for the dyes under discussion are given in Table I. Although it may be coincidental, dyes 18 and 19 absorb at the same wavelength as the straight chain pentamethine dye 1.

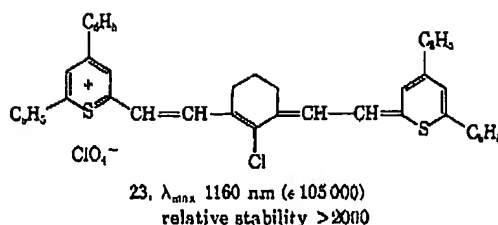
In order to determine the stabilizing effect of the chain rings, the stability of the dyes was determined by irradiating a sample (optical density 1 in 1,2-dichloroethane) with the light source of a Cary Model 14 spectrophotometer equipped with a filter to eliminate light below 650 nm. The stabilities of the dyes are compared on a relative basis in Table I using 1 as the basis of comparison.

We had made the assumption in our attempts to synthesize stable heptamethine pyrylium dyes that an increase in the number of methine groups that are contained in rings should result in more stable dyes. It was, therefore, with great interest that we noted that 15 (relative stability 78) was as stable as the corresponding dye 5. We decided to prepare other examples similar to 15, and the following compounds were synthesized.



The λ_{max} of these compounds again illustrate the bathochromic shift caused by a five-membered ring and also that alkyl groups at the 1 and 7 positions of the chain result in a small bathochromic shift. Evidently compound 21 is in a crowded configuration since the ϵ value is only about $\frac{1}{2}$ the value of similar dyes. We have not measured the relative stability of 21 but predict that it will be relatively unstable. Compound 22 was rather interesting. The first time the absorption spectrum was measured, there was no absorption in the near infrared. After we received the elemental analysis and were convinced that the compound had been obtained, the absorption spectrum was rechecked. It was found that if a 5×10^{-5} M solution of the dye in CH_2Cl_2 was placed in the spectrophotometer, which was set at 1100 nm, the optical density dropped from approximately 1 to zero in less than 1 min. We can offer no plausible explanation for the greater instability of 22 compared to 21.

Since thiapyrylium salts absorb at longer wavelengths than the corresponding pyrylium salts, an example of a hepta-



methine thiapyrylium dye was prepared to determine the magnitude of the effect. The dye 23 showed a substantial (88 nm) bathochromic shift in comparison with the corresponding pyrylium dye 15. The most unusual effect, however, was the large increase in stability relative to pyrylium dyes.

We believe that the best way to obtain large bathochromic shifts in the heptamethine dyes would be through replacement of the chlorine atom at the center of the chain with a more electronegative atom or group, but the only example we have been able to prepare is the bromo derivative 24 (see Table I), which showed absorption and stability very similar to those of the corresponding chloro derivative 10.

Experimental Section

8-[5-(6,7-Dihydro-2,4-diphenyl-5H-1-benzopyran-8-yl)-2,4-trimethylene-2,4-pentadienyldiene]-5,6,7,8-tetrahydro-2,4-diphenyl-1-benzopyrylium Perchlorate (5). All runs were carried out on a 5-mmol scale except where indicated. A mixture of 1.9 g (0.005 mol) of 2,4-diphenyl-5,6,7,8-tetrahydro-1-benzopyrylium perchlorate⁸ (4), 0.81 g (0.0025 mol) of 2, 0.4 g (0.005 mol) of sodium acetate, 20 ml of acetic acid, and 15 ml of acetic anhydride was refluxed for 15 min, and after chilling, the solid was collected, washed with water and then alcohol, and recrystallized from nitromethane, yield 1.4 g, mp 291–292 °C dec. The λ_{max} ($\epsilon \times 10^{-3}$) in CH_2Cl_2 are 510 (30.0), 620 (6.0), 690 (4.0), ~880 (35.0), 985 (92.0), and 1090 nm (149.0).

Anal. Calcd for $\text{C}_{60}\text{H}_{44}\text{ClO}_6$: C, 77.5; H, 5.6. Found: C, 77.3; H, 5.5.

8-[5-(6,7-Dihydro-2,4-diphenyl-5H-1-benzopyran-8-yl)-2,4-dimethylene-2,4-pentadienyldiene]-5,6,7,8-tetrahydro-2,4-diphenyl-1-benzopyrylium perchlorate (6) was prepared from 4 and 3, 3-mmol scale, yield 0.5 g (not recrystallized), mp 225–227 °C. The λ_{max} ($\epsilon \times 10^{-3}$) in CH_2Cl_2 are 360 (17.8), 510 (9.1), ~660 (6.5), 640 (4.5), 1005 (38.5), and 1138 nm (70.0).

Anal. Calcd for $\text{C}_{49}\text{H}_{41}\text{ClO}_6$: C, 77.3; H, 5.4. Found: C, 77.0; H, 5.7.

2-Chloro-1-formyl-3-hydroxymethylcyclohexene (8). A solution of 40 ml of dimethylformamide in 40 ml of methylene chloride was chilled in an ice bath and 37 ml of phosphorus oxychloride in 35 ml of methylene chloride was added dropwise with stirring, followed by 10 g of cyclohexanone. The solution was refluxed for 3 h, cooled, poured onto 200 g of ice, and allowed to stand overnight. The yellow solid was collected and dried, yield 16 g, mp 125–127 °C. A sample was recrystallized from a small volume of acetone cooled with dry ice, to give material melting at 130–131 °C.

Anal. Calcd for $\text{C}_6\text{H}_9\text{ClO}_2$: C, 55.7; H, 5.3; Cl, 20.5. Found: C, 55.4; H, 5.4; Cl, 20.4.

8-[5-(6,7-Dihydro-2,4-diphenyl-5H-1-benzopyran-8-yl)-3-chloro-2,4-trimethylene-2,4-pentadienyldiene]-5,6,7,8-tetrahydro-2,4-diphenyl-1-benzopyrylium Perchlorate (10). The general procedure was used with 4 and 8 giving 1.9 g of 10, mp 234–235 °C (from nitromethane). The λ_{max} ($\epsilon \times 10^{-3}$) in CH_2Cl_2 are 360 (27.0), 500 (21.0), 530 (22.8), 620 (5.7), 695 (3.8), 1000 (67.5), and 1120 nm (113.0).

Anal. Calcd for $\text{C}_{60}\text{H}_{43}\text{Cl}_2\text{O}_6$: C, 74.2; H, 5.2. Found: C, 74.2; H, 5.3.

8-[5-(6,7-Dihydro-2,4-diphenyl-5H-1-benzopyran-8-yl)-3-chloro-2,4-dimethylene-2,4-pentadienyldiene]-5,6,7,8-tetrahydro-2,4-diphenyl-1-benzopyrylium Perchlorate (11). Compound 11 was prepared by the general procedure for 4 and 9, yield 1.7 g, mp 240–242 °C (from nitromethane). The λ_{max} ($\epsilon \times 10^{-3}$) in CH_2Cl_2 are 365 (22.0), 530 (17.0), 632 (10.5), 1012 (73.5), and 1145 nm (143.0).

Anal. Calcd for $\text{C}_{49}\text{H}_{40}\text{Cl}_2\text{O}_6$: C, 74.0; H, 5.1. Found: C, 74.2; H, 5.0.

7-[5-(2,4-Diphenyl-5,6-dihydrocyclopenta[b]pyran-7-yl)-

3-chloro-2,4-trimethylene-2,4-pentadienyldiene]-2,4-diphenyl-5,7-dihydro-5*H*-cyclopenta[*b*]pyrylium Perchlorate (12). The general procedure was used with 2,4-diphenylcyclopenta[*b*]pyrylium perchlorate and 8 and the yield of dye was 2 g, mp 245–247 °C. The λ_{max} ($\epsilon \times 10^{-3}$) in CH_2Cl_2 are 375 (17.6), ~510 (12.0), 530 (14.8), 630 (6.7), 722 (2.0), 1010 (56.0), and 1152 nm (120.0).

Anal. Calcd for $\text{C}_{48}\text{H}_{38}\text{Cl}_2\text{O}_6$: C, 73.7; H, 4.9. Found: C, 73.5; H, 5.0.

7-[5-(2,4-Diphenyl-5,6-dihydrocyclopenta[*b*]pyran-7-yl)-3-chloro-2,4-dimethylene-2,4-pentadienyldiene]-2,4-diphenyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyrylium Perchlorate (13). The yield of dye, prepared from 2,4-diphenylcyclopenta[*b*]pyrylium perchlorate and 9 in the usual manner, was 1.9 g, mp 248–250 °C. The λ_{max} ($\epsilon \times 10^{-3}$) in CH_2Cl_2 are 368 (32.0), 550 (12.0), 670 (11.0), 1030 (46.0), and 1180 nm (112.0).

Anal. Calcd for $\text{C}_{47}\text{H}_{36}\text{Cl}_2\text{O}_6$: C, 73.5; H, 4.7. Found: C, 73.6; H, 4.8.

8-[5-(6,7-Dihydro-2,4-diphenyl-5*H*-1-benzopyran-8-yl)-3-chloro-2,4-(2-*tert*-butyltrimethylene-2,4-pentadienyldiene)-5,6,7,8-tetrahydro-2,4-diphenyl-1-benzopyrylium Perchlorate (14). Compound 14 was prepared from 4 and 5-*tert*-butyl-2-chloro-1-formyl-3-hydroxymethylenecyclohexane (prepared as described for 8, mp 122–123 °C) by the general procedure, yield 1.2 g, mp 247–248 °C (from nitromethane). The λ_{max} ($\epsilon \times 10^{-3}$) in CH_2Cl_2 are 360 (27.0), 500 (21.0), 530 (23.8), 620 (7.6), 680 (4.3), 1000 (65.0), and 1120 nm (110.0).

Anal. Calcd for $\text{C}_{54}\text{H}_{40}\text{Cl}_2\text{O}_6$: C, 75.0; H, 5.7; Cl, 8.2. Found: C, 75.0; H, 6.0; Cl, 8.1.

2-[7-(4,6-Diphenyl-2*H*-pyran-2-ylidene)-4-chloro-3,5-trimethylene-1,3,5-heptatrienyl]-4,6-diphenylpyrylium Perchlorate (15). Compound 15 was prepared from 8 and 2-methyl-4,6-diphenylpyrylium perchlorate, yield 2.1 g, mp 220–221 °C. The λ_{max} ($\epsilon \times 10^{-3}$) in CH_2Cl_2 are 370 (22.5), 505 (13.3), 610 (6.7), 670 (3.6), 950 (63.0), 1072 nm (107.0).

Anal. Calcd for $\text{C}_{44}\text{H}_{34}\text{Cl}_2\text{O}_6$: C, 72.4; H, 4.7. Found: C, 72.0; H, 4.8.

8-[5-(6,7-Dihydro-2,4-diphenyl-5*H*-1-benzopyran-8-yl)-2,4-(1,2-phenylene)-2,4-pentadienyldiene]-5,6,7,8-tetrahydro-2,4-diphenyl-1-benzopyrylium perchlorate (18) was prepared from 4 and 16, yield 1.8 g, mp 245–247 °C (from acetic anhydride). The λ_{max} ($\epsilon \times 10^{-3}$) in methylene chloride are 1042 (185.0), 930 (51.0), 615 (5.2), 565 (4.3), 518 (6.3), 395 (11.5), 335 (24.8), 285 (29.0), and 250 nm (25.4).

Anal. Calcd for $\text{C}_{53}\text{H}_{41}\text{ClO}_6$: 78.7; H, 5.1; Cl, 4.4. Found: C, 78.5; H, 5.2; Cl, 4.3.

8-[5-(6,7-Dihydro-2,4-diphenyl-5*H*-1-benzopyran-8-yl)-3-chloro-2,4-(1,2-phenylene)-2,4-pentadienyldiene]-5,6,7,8-tetrahydro-2,4-diphenyl-1-benzopyrylium perchlorate (19) was prepared from 4 and 17, yield 2 g, mp 226–277 °C (from a mixture of acetic anhydride and acetic acid). The λ_{max} ($\epsilon \times 10^{-3}$) in methylene chloride are 1040 (175.0), 930 (70.0), 515 (9.0), 465 (8.0), 418 (11.0), 300 (14.0), 336 (24.5), and 290 nm (42.0).

Anal. Calcd for $\text{C}_{53}\text{H}_{40}\text{Cl}_2\text{O}_6$: C, 75.4; H, 4.8; Cl, 8.4. Found: C, 75.1; H, 5.0; Cl, 8.0.

2-[7-(4,6-Diphenyl-2*H*-pyran-2-ylidene)-4-chloro-3,5-dimethylene-1,3,5-heptatrienyl]-4,6-diphenylpyrylium perchlorate (20) was prepared from 2-methyl-4,6-diphenylpyrylium perchlorate and 3, yield 0.8 g, mp 214–215 °C dec (from acetic acid plus acetic anhydride). The λ_{max} ($\epsilon \times 10^{-3}$) in methylene chloride are 1095 (167.0), 970 (107), 610 (21.3), 530 (25.6), 365 (42.8), 315 (87.3), and 285 nm (37.0).

Anal. Calcd for $\text{C}_{45}\text{H}_{32}\text{Cl}_2\text{O}_6$: C, 72.7; H, 4.5; Cl, 9.9. Found: C, 72.4; H, 4.6; Cl, 9.6.

2-[8-(4,6-Diphenyl-2*H*-pyran-2-ylidene)-5-chloro-4,6-dimethylene-2,4,6-nonatrien-2-yl]-4,6-diphenylpyrylium perchlorate (21) was prepared from 2-ethyl-4,6-diphenylpyrylium

perchlorate and 3, yield 0.9 g, mp 220–222 °C dec (from a mixture of acetic anhydride and acetic acid). The λ_{max} ($\epsilon \times 10^{-3}$) in methylene chloride are 1110 (52.8), 1056 (54.0), 635 (6.6), 560 (9.2), 520 (11.0), and 380 nm (32.0).

Anal. Calcd for $\text{C}_{46}\text{H}_{36}\text{Cl}_2\text{O}_6$: C, 72.7; H, 4.9; Cl, 9.6. Found: C, 72.5; H, 4.8; Cl, 9.5.

2-[8-(4,6-Diphenyl-2*H*-pyran-2-ylidene)-5-chloro-4,6-trimethylene-2,4,6-nonatrien-2-yl]-4,6-diphenylpyrylium perchlorate (22) was prepared from 2-ethyl-4,6-diphenylpyrylium perchlorate and 2, yield 2.0 g, mp 227–229 °C dec (from a mixture of acetic anhydride and acetic acid).

Anal. Calcd for $\text{C}_{46}\text{H}_{36}\text{Cl}_2\text{O}_6$: C, 72.9; H, 7.3; Cl, 9.4. Found: C, 73.0; H, 7.1; Cl, 9.3.

2-[7-(4,6-Diphenyl-2*H*-thiopyran-2-ylidene)-4-chloro-3,5-trimethylene-1,3,5-heptatrienyl]-4,6-diphenylthiopyrylium perchlorate (23) was prepared from 2-methyl-4,6-diphenylthiopyrylium perchlorate and 2, yield 2.1 g, mp 236–238 °C (from acetic anhydride). The λ_{max} ($\epsilon \times 10^{-3}$) in methylene chloride are 1160 (105.0), 1038 (74.5), 630 (7.0), 530 (13.2), and 380 nm (23.6).

Anal. Calcd for $\text{C}_{44}\text{H}_{34}\text{Cl}_2\text{O}_4\text{S}_2$: C, 69.4; H, 4.6. Found: C, 69.3; H, 4.3.

8-[5-(6,7-Dihydro-2,4-diphenyl-5*H*-1-benzopyran-8-yl)-3-bromo-2,4-trimethylene-2,4-pentadienyldiene]-5,6,7,8-tetrahydro-2,4-diphenyl-1-benzopyrylium Perchlorate (24). To 100 ml of DMF which was stirred in an ice bath was added 17 g of POBr_3 . A white precipitate separated. The mixture was stirred for 30 min at room temperature, 2 g of cyclohexanone was added, and then the mixture was heated for 1 h on a steam bath. There was still undissolved material present so the mixture was heated by a heating mantle until the solid dissolved, and the solution was cooled and then poured into water. After standing overnight, the pale yellow solid was collected, washed with water, and dried, yield 2 g, mp 185–186 °C. The IR of the solid was very similar to that of 2. Compound 24 was prepared from this material and 4, yield 1.5 g, mp 223–224 °C (from nitromethane).

Anal. Calcd for $\text{C}_{50}\text{H}_{42}\text{BrClO}_6$: C, 70.3; H, 5.0; Br, 9.4. Found: C, 69.9; H, 4.9; Br, 9.2.

Registry No.—1, 22371-56-8; 2, 61009-98-1; 3, 61009-97-0; 4, 16997-44-1; 5, 61010-01-3; 6, 61010-03-5; 8, 61010-04-6; 9, 61010-05-7; 10, 61010-07-9; 11, 61010-09-1; 12, 61010-11-5; 13, 61010-13-7; 14, 61010-15-9; 15, 61047-19-8; 16, 61010-16-0; 17, 61010-17-1; 18, 61010-19-3; 19, 61010-21-7; 20, 61010-23-9; 21, 61010-25-1; 22, 61010-27-3; 23, 61010-29-5; 24, 61010-31-9; dimethylformamide, 68-12-2; phosphorus oxychloride, 10025-87-3; cyclohexanone, 108-94-1; 2,4-diphenylcyclopenta[*b*]pyrylium perchlorate, 21016-30-8; 5-*tert*-butyl-2-chloro-1-formyl-3-hydroxymethylenecyclohexane, 61009-99-2; 2-methyl-4,6-diphenylpyrylium perchlorate, 7654-52-6; 2-ethyl-4,6-diphenylpyrylium perchlorate, 18223-01-8; 2-methyl-4,6-diphenylthiopyrylium perchlorate, 41494-44-4.

References and Notes

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